PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	**FOR FURTHER ACTION** see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
P56885P		
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/GB 97/03140	14/11/1997	21/11/1996
Applicant		
DALGETY PLC et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. [ ] **Certain claims were found unsearchable** (see Box I).

2. [ ] **Unity of invention is lacking** (see Box II).

3. [ ] The international application contains disclosure of a **nucleotide and/or amino acid sequence listing** and the international search was carried out on the basis of the sequence listing
   - [ ] filed with the international application.
   - [ ] furnished by the applicant separately from the international application,
     - [ ] but not accompanied by a statement to the effect that it did not include matter going beyond the disclosure in the international application as filed.
   - [ ] Transcribed by this Authority

4. With regard to the **title,**
   - [X] the text is approved as submitted by the applicant
   - [ ] the text has been established by this Authority to read as follows:

5. With regard to the **abstract,**
   - [X] the text is approved as submitted by the applicant
   - [ ] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this International Search Report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is:

   Figure No. _____
   - [ ] as suggested by the applicant.
   - [ ] because the applicant failed to suggest a figure.
   - [ ] because this figure better characterizes the invention.
   - [X] None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 97/03140

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08B37/14 C08B37/06 A61L15/60 A21D2/36 A23L1/052

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 338 452 A (CULTOR LTD.) 25 October 1989 see claim 1	1-29
Y	EP 0 126 394 A (PHILLIPS PETROLEUM COMPANY) 28 November 1984 see page 2, line 13 - line 18	1-29
Y	GB 2 261 671 A (GB BIOTECHNOLOGY LIMITED) 26 May 1993 cited in the application see claims 1,2	1-29
A	WO 96 03440 A (NOVO NORDISK) 8 February 1996 cited in the application	

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
27 February 1998	11/03/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Lensen, H

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 97/03140

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 97 17492 A (NOVO NORDISK A/S) 15 May 1997 see page 10, line 16 - line 17	1

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 97/03140

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 338452 A	25-10-89	CA 1335635 A	23-05-95
		DK 188389 A	23-10-89
		JP 1312956 A	18-12-89
		NO 177212 B	02-05-95
		US 4990343 A	05-02-91
EP 126394 A	28-11-84	CA 1228431 A	20-10-87
		DE 3466974 A	03-12-87
		DK 237384 A	14-11-84
		JP 1018794 B	07-04-89
		JP 1533912 C	12-12-89
		JP 59213494 A	03-12-84
		US 4485016 A	27-11-84
GB 2261671 A	26-05-93	BG 98769 A	30-06-95
		CA 2123602 A	27-05-93
		EP 0646135 A	05-04-95
		EP 0612326 A	31-08-94
		FI 942245 A	13-05-94
		HU 67479 A	28-04-95
		JP 7501216 T	09-02-95
		JP 7502057 T	02-03-95
		NO 941813 A	13-05-94
		US 5530112 A	25-06-96
		US 5633032 A	27-05-97
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		AU 2948892 A	15-06-93
		WO 9310157 A	27-05-93
		WO 9310158 A	27-05-93
		ZA 9208825 A	21-06-93
WO 9603440 A	08-02-96	AU 3074595 A	22-02-96
		CA 2195640 A	08-02-96
		CZ 9700205 A	14-05-97
		EP 0750641 A	02-01-97
		FI 970274 A	23-01-97
WO 9717492 A	15-05-97	AU 7560996 A	29-05-97

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

PRICE, Vincent A.
FRY HEATH & SPENCE
The Old College
53 High Street
Horley, Surrey RH6 7BN
GRANDE BRETAGNE

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NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY EXAMINATION REPORT
(PCT Rule 71.1)

Date of mailing *(day/month/year)*	24. 11. 98
Applicant's or agent's file reference: P56885P	IMPORTANT NOTIFICATION

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/GB97/03140	14/11/1997	21/11/1996

Applicant
DALGETY PLC et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.

2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.

3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. **REMINDER**

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/	Authorized officer
European Patent Office D-80298 Munich Tel. (+49-89) 2399-0, Tx: 523656 epmu d Fax: (+49-89) 2399-4465	Hingel, W Tel. (+49-89) 2399-8235

Form PCT/IPEA/416 (July 1992)

19

PATENT COOPERATION TREATY

REC'D 26 NOV 1998
WIPO PCT

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (PCT/IPEA/416)
P56885P		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/GB97/03140	14/11/1997	21/11/1996
International Patent Classification (IPC) or national classification and IPC		
C08B37/14		
Applicant		
DALGETY PLC et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 5 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 5 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
05/06/1998	24. 11. 98
Name and mailing address of the IPEA/	Authorized officer
European Patent Office D-80298 Munich Tel. (+49-89) 2399-0, Tx: 523656 epmu d Fax: (+49-89) 2399-4465	Kairi, M Telephone No. (+49-89) 2399-8672

Form PCT/IPEA/409 (Cover sheet) (January 1994)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB97/03140

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-17	as originally filed				

Claims, No.:

1-29	as received on	31/10/1998	with letter of	28/10/1998	

2. The amendments have resulted in the cancellation of:

☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-29
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-29
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-29
	No:	Claims	

2. Citations and explanations

see separate sheet

Re Item V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Article 33(2) PCT

None of the prior art discloses a hemicellulosic material comprising an oxidase supplement and a peroxidase supplement.

Article 33(3) PCT

The document WO-A-96/03440(D2) discloses a method for causing gelling or increase of viscosity of an aqueous medium containing a gellable polymeric material having sunstituents with phenolic hydroxy groups which comprises adding an oxidase, particularly a laccase, to the aqueous medium (Abstract). Phenolic polysaccharides include arabinoxylans having ferulyl groups obtainable from cereals such as the flour or bran of cereals and pectins (page 6). Gelled products or products of increased viscosity have applications in the food and feed areas, the pharmaceutical and medical areas such as a material for a wound or burn dressing and agricultural areas (page 1, line 25 to page 2, line 7; page 11, lines 8-12). That prior art uses an oxidase to directly oxidise gellable polymeric materials in the absence of hydrogen peroxide and peroxidases(see page 3, lines 22-26 and lines 27-30) and oxygen is the oxidising agent. Oxidases are relatively weak oxidation-promoters and the range of different gel strengths obtainable by the use of such enzymes is limited.

The document GB-A-2 261 671(D3) discloses a method of producing gel material which comprises firstly providing an aqueous soluble hemicellulosic starting medium which is free of glucans and obtainable from testaceous plant material which is then reacted with an oxidising system comprising at least one peroxide together with at least one oxygenase such as a peroxidase. According to that document the peroxide is added as a reactant and is not produced by the in situ generation by redox enzymes.

The subject-matter of Claim 1 of the present application differs from that disclosure in that the hemicellulosic material comprises a peroxidase supplement in addition to the oxidase supplement. Thus there are a coupled series of reactions, the first being the oxidation (by an oxidase) of an oxidase substrate (preferably glucose) to produce hydrogen peroxide, the second being the oxidative gelation of the hemicellulosic material mediated by a peroxidase and fuelled by the hydrogen peroxide produced in the first reaction.The invention avoids the danger of explosion associated with excess

of hydrogen peroxide by a negative feedback loop which acts to ensure that if temperature rises due to excessive hydrogen peroxide production then the enzymes producing the hydrogen peroxide progressively denature.

The object of the present invention is to provide an effective gelation system of hemicellulosic material which yields a vast range of gel strengths and which is devoid of the inconveniences of using pre-formulated hydrogen peroxide preparations as a reactant.

The solution provided is non-obvious, since there is nothing in the prior art to suggest that oxidase/peroxidase reactions could be effectively coupled, such that adequate concentrations of hydrogen peroxide could be generated at a sufficient rate such that a hemicellulosic material could be efficiently oxidatively gelled and also there is no indication in the prior art of the advantages indicated above of using the gelation system according to the present application and furthermore document D2 teaches away from the present invention as indicated above.

CLAIMS

1. A hemicellulosic material comprising an oxidase supplement, a peroxidase supplement and optionally an oxidase substrate supplement.

2. The material of claim 1 wherein:
   (a) the oxidase is glucose oxidase; and/or
   (b) the peroxidase is horse radish peroxidase; and/or
   (c) the oxidase substrate supplement is glucose.

3. The material of claim 1 or claim 2 wherein the hemicellulosic material is derived from cereal flour, husk or bran, or from legumes (e.g. from maize, wheat, barley, rice, oats or malt).

4. The material of any one of claims 1-3 wherein the hemicellulosic material comprises a pentosan, e.g. a water soluble or alkali soluble pentosan fraction.

5. The material of claim 4 wherein the pentosan comprises arabinoxylan, for example, arabinoxylan ferulate.

6. The material of claim 5 wherein the hemicellulosic material consists or consists essentially of arabinoxylan ferulate.

7. The material of any one of the preceding claims in the form of a powder, for example a substantially anhydrous powder and optionally a dispersant (e.g. glucose or maltodextrin).

8. The material of claim 7 which comprises oxidase, oxidase substrate (e.g. glucose) and optionally peroxidase supplements, the material

being self-gelling on the addition of water.

9. The material of any one of claims 1-8 in the form of an aqueous solution.

10. The material of claim 9 which is substantially oxygen free.

11. The material of claim 10 which comprises oxidase, oxidase substrate (e.g glucose) and optionally peroxidase supplements and which is self-gelling on exposure to oxygen.

12. A gel or viscous medium comprising the material of any one of claims 1-11 which has been oxidatively gelled.

13. The gel of claim 12 wherein the material comprises or consists essentially of cross linked arabinoxylan.

14. The gel of viscous medium of claim 12 or 13 in dehydrated form.

15. The dehydrated gel or viscous medium of claim 14 in rehydrated form.

16. A process for preparing a gel or viscous medium comprising the step of oxidatively gelling the material of any one of claims 1-11, for example by adding water to the material of claim 8 or by exposing the material of any one of claims 9-11 to oxygen.

17. A process for effecting oxidative gelation of a hemicellulosic material comprising the step of promoting the generation of hydrogen peroxide *in situ* with redox enzymes, wherein the redox enzymes comprise an oxidase and a peroxidase.

18. The process of claim 17 wherein the oxidase is horse radish

peroxidase and/or the oxidase is glucose oxidase.

19. The process of claim 17 or 18 wherein the process comprises the steps of supplementing a hemicellulosic material with an oxidase and optionally an oxidase substrate and/or a peroxidase.

20. The process of any one of claims 17-19 wherein the generation of hydrogen peroxide is promoted by:

(a) providing oxygen to the material (e.g. by generation or release *in situ*); and/or

(b) providing water to the material; and/or

(c) providing oxidase substrate to the material (e.g. by generation or release *in situ*); and/or

(d) activating one or more of the redox enzymes (e.g. chemically or physically),

wherein the provision of oxygen or substrate may be by controlled release or generation *in situ*, for example by triggered generation or release by heat, irradiation or chemical treatment(s).

21. A gel or viscous medium produced by (or obtainable by) the process of any one of claims 16-20.

22. A process for producing a hemicellulosic material (for example a material according to any one of claims 1-11) comprising the step of supplementing a hemicellulose with an oxidase (e.g. glucose oxidase) and a peroxidase (e.g. horse radish peroxidase) supplement.

23. A material produced by (or obtainable by) the process of claim 22.

24. A pharmaceutical or cosmetic preparation or medical device comprising the material, gel, viscous medium, dehydrated gel/viscous medium of any one of the preceding claims, the preparation or device being for example selected from: a wound plug, wound dressing, controlled release device, an encapsulated medicament or drug, a lotion, cream, suppository, pessary, spray, artificial skin, protective membrane, a neutraceutical, prosthetic, orthopaedic, ocular insert, injectant, lubricant or cell implant matrix, optionally further comprising an antibiotic, analgesic and/or anti-inflammatory agent.

25. The material, gel or viscous medium of any one of the preceding claims for use in therapy, prophylaxis or diagnosis, for example in the treatment of skin lesions (e.g. burns, abrasions or ulcers).

26. A wound dressing comprising the material of claim 11, for example in the form of a spray.

27. A bread improver comprising the material, gel or viscous medium of any one of the preceding claims.

28. A foodstuff, dietary fibre source, food ingredient, additive, lubricant, supplement or dressing comprising the material of any one of claims 1-11, 23 or 25, the gel or viscous medium of any one of claims 12-14, 21 or 25, for example being selected from a petfood (wherein the gel e.g. acts as a binder), a flavour delivery agent, a canning gel, fat replacer (e.g. comprising macerated gel of any one of the preceding claims), a coating, a glaze, a bait or a gelatin replacer.

29. A masking agent comprising the gel of any one of the preceding claims, for example for use in masking semiconductor wafers, etching plates or surfaces to be painted.

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
C08B 37/14, 37/06, A61L 15/60, A21D 2/36, A23L 1/052

A1

(11) International Publication Number: WO 98/22513

(43) International Publication Date: 28 May 1998 (28.05.98)

(21) International Application Number: PCT/GB97/03140

(22) International Filing Date: 14 November 1997 (14.11.97)

(30) Priority Data:

9624204.5	21 November 1996 (21.11.96)	GB
9718072.3	28 August 1997 (28.08.97)	GB

(71) Applicant *(for all designated States except US)*: DALGETY PLC [GB/GB]; 100 George Street, London W1H 5RH (GB).

(72) Inventor; and

(75) Inventor/Applicant *(for US only)*: FITCHETT, Colin, Stanley [GB/GB]; 13 Sedgwick Street, Cambridge CB1 3AJ (GB).

(74) Agents: PRICE, Vincent, Andrew et al.; Fry Heath & Spence, The Old College, 53 High Street, Horley, Surrey RH6 7BN (GB).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published

With international search report.

(54) Title: PRODUCTION OF VEGETABLE GELS

(57) Abstract

Described are hemicellulose–based gels and viscous media, processes for their production, products containing such gels and/or viscous media and various applications thereof. Improved methods for performing oxidative gelation of hemicelluloses which avoid the need for the addition of hydrogen peroxide are also described.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

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PRODUCTION OF VEGETABLE GELS

The present invention relates to hemicellulose-based gels and viscous media, to processes for their production, to products containing such gels and/or viscous media and to various applications thereof. In particular, the present invention relates to an improved method for performing oxidative gelation of hemicelluloses which avoids the need for the addition of hydrogen peroxide.

Plant tissue, especially cell wall material, contains hemicelluloses. The term "hemicellulose" is a term of art used to embrace non-cellulosic, non-starch plant polysaccharides. The term therefore embraces *inter alia* pentosans, pectins and gums.

Some hemicelluloses are suitable as substrates for oxidative gelation ("gelling hemicelluloses"): such hemicelluloses often have substituents with phenolic groups which are cross-linkable with certain oxidizing agents.

Arabinoxylan and pectin constitute two particularly important classes of hemicellulose. Arabinoxylans consist predominantly of the pentoses arabinose and xylose, and are therefore often classified as pentosans. However, in many cases hexoses and hexuronic acid are present as minor constituents, and therefore they may also be referred to descriptively as heteroxylans.

The arabinoxylan molecule consists of a linear backbone of (1-4)-ß-xylopyranosyl units, to which substituents are attached through 02 and 03 atoms of the xlosyl residues. The major substituents are single α-L-arabinofuranosyl residues. Single α-D-glucoronopyranosyl residues and their 4-O-methyl ethers are also common substituents.

Arabinoxylan preparations are usually heterogenous with respect to the ratio of xylose to arabinose (i.e. the degree of substitution) and in the pattern of substitution of the arabinosyl units along the (1-4)-ß-xylan backbone.

Phenolic acid (including ferulic acid) and acetyl substituents occur at intervals along the arabinoxylan chains. These substituents to some extent determine the solubility of the arabinoxylan. Arabinoxylan preparations bearing phenolic (e.g. ferulic acid substituents) are referred to herein as "AXF", while those bearing acetyl substituents are designated "AXA". Similarly, preparation bearing both phenolic (e.g. ferulic acid) and acetyl substituents are hereinafter abbreviated to the designation "AXFA". Arabinoxylan preparations having few phenolic (e.g. ferulic acid) substituents are designated "AX": when the degree of substitution falls below that required for oxidative gelation, the arabinoxylan is designated a "non-gelling arabinoxylan" (a term which therefore embraces AX and AXA).

Pectins constitute another important class of hemicelluloses. As used herein and unless otherwise indicated, the term "pectin" is used *sensu lato* to define hemicellulose polymers rich in D-galacturonic acid. Many (but not all) are cell wall components. The term "pectin" is also used herein *sensu stricto* to define the so-called "true pectins", which are characterised by the presence of an O-(*α*-D-galacturonopyranosyl)-(1-2)-L-rhamnopyranosyl linkage within the molecule.

The pectins may be subcategorized on the basis of their structural complexity. At one extreme are "simple pectins", which are galacturonans. At the other extreme are "complex pectins" exemplified by rhamnogalacturonan II, which contains at least 10 different monosaccharide components in the main chain or as a components of branches. Pectins of intermediate complexity (herein referred to as "mesocomplex pectins" contain alternate rhamnose and galacturonic acid units, while others have

branches of glucoronic acid linked to galacturonic acid.

Complex and mesocomplex pectins are made up of "smooth" regions (based on linear homogalacturonan) and "hairy" regions corresponding to the rhamnogalacturonan backbone with side-branches of varying length.

Certain pectins (for example, pectins obtainable from representatives of the plant family *Chenopodiaceae*, which include beets (e.g. sugar beet), spinach and mangelwurzels) are substituted to some extent with substituents derived from carboxylic acids (usually substituted cinnamic acids) containing phenolic groups. Such pectins may be oxidatively cross-linked to produce viscous solutions or gels via their phenolic substituents. This can be achieved by powerful oxidants (e.g. persulfate - see J. - F. Thibault *et alia*, in The Chemistry and Technology of Pectin, Academic Press 1991, Chapter 7, pages 119-133) or a combination of peroxidase and hydrogen peroxide (see Thibault *et alia*, *ibidem*). FR 2 545 101 A1 also describes the gelling of beet pectins using an oxidant (e.g. hydrogen peroxide) and an enzyme (peroxidase). Such pectins are referred to herein as "gelling pectins".

Sugar beet pectin is especially rich in arabinan. Arabinan contains ß-1, 5-linked arabinose in the backbone with α-(1->3) or α-(1->2) - linked arabinose residues, whereas arabinogalactan contains ß-1, 4-linked galactose in the backbone, with α-(1->3) or α-(1->2) linked arabinose residues. Feruloyl substituents are linked to the arabinose and/or the galactose in the arabinan and arabinogalactan side-branches of the rhamnogalacturonan part. The "ferulic acid" content varies according to the extraction method, but is often about 0.6%.

Beet pectins obtained by processes which partially remove arabinose residues may exhibit improved gelling properties. Thus, procedures involving mild acid treatment and/or treatment with an α-arabinofuranosidase will

improve the gelling properties of the pectin (see F. Guillon and J. -F. Thibault, *ibidem*). Such pectins are hereinafter referred to as "treated pectins". Hemicelluloses are complex mixtures of noncellulosic cell wall polysaccharides, including pentosans such as arabinoxylans. Convenient sources of hemicelluloses include cereals (such as maize, barley, wheat, oats, rice), pulses (e.g. soya), legumes and fruit.

There are many known methods for fractionating plant material (such as testaceous or cell wall material) to produce hemicellulose and cellulose fractions. Such methods usually involve alkali or water extraction to yield insoluble cellulose and soluble hemicellulose fractions, followed by separation. The soluble extract is then often neutralized (or acidified) to precipitate hemicelluloses. Organic solvents are also commonly used instead of (or in addition to) acidification to precipitate further hemicellulose fractions.

Aqueous extracts of many hemicellulose fractions are known to form gels (or viscous media) when treated with oxidizing agents. The phenomenon is known as "oxidative gelation" in the art, but the term is used herein in a somewhat broader sense to include the case where viscous solutions are produced rather than true gels. This reflects the fact that oxidative gelation is a progressive phenomenon which may be controlled to vary the degree of gelation to the extent that hard, brittle gels are formed at one extreme and slurries, gravies or viscous liquids at the other.

The biochemical basis of the gelling process is not yet fully understood. However, gel formation and/or viscosity increases are thought to arise (at least in part) from cross linking within and/or between macromolecular components of the hemicellulose mediated by ferulic acid residues (for example, involving diferulate generated by oxidative coupling of the aromatic nucleus of ferulic acid). These ferulic acid residues occur on arabinoxylans present in the hemicellulose. Extensive hydrolysis (by e.g.

harsh alkaline treatments) is known to strip the ferulic acid residues from the bulk pentosans, and so hemicelluloses for use as starting materials in the production of gels or viscous solutions are usually extracted by water (particularly hot water) or mild alkali extraction.

As used herein (and as is usual in the art), the terms "ferulic acid" and "ferulate" are used *sensu lato* encompass feruloyl (often denoted feruloyl) groups (i.e. 4-hydroxy-3-methoxy-cinnamyl groups) and derivatives (particularly oxidized derivatives) thereof.

Only a few oxidizing agents are known to have the ability to induce gelation, and these include hydrogen peroxide (usually in conjunction with a peroxidase), ammonium persulphate and formamidine disulphide.

WO 96/03440 describes the use of an oxidase (preferably a laccase) for promoting oxidative gelation of *inter alia* arabinoxylans. However, laccase may not be acceptable for use in certain food applications, is relatively expensive and the supply is limited. Moreover, oxidases such as laccase are relatively weak oxidation-promoters, and the range of different gel strengths obtainable by the use of such enzymes is limited. Indeed it is possible that the crosslinking achieved through the use of laccase and other oxidases differs fundamentally from that mediated by e.g. hydrogen peroxide, so that the gels may differ significantly in structure from those produced by other forms of oxidative gelation.

WO 93/10158 describes oxidative gelation of hemicellulosic material using an oxidizing system comprising a peroxide (such as hydrogen peroxide) and an oxygenase (such as a peroxidase). However, hydrogen peroxide is inconvenient as a reagent in industrial-scale processes, and is potentially dangerous.

There is therefore a need for alternative methods of promoting

oxidative gelation which avoid the aforementioned problems.

Thus, according to the present invention there is provided a hemicellulosic material comprising an oxidase (e.g. glucose oxidase) and optionally a peroxidase (e.g. horse radish peroxidase) supplement.

The hemicellulose/hemicellulosic material for use in the invention may be any hemicellulose meeting the definition set out earlier. In particular, the hemicellulose may be an arabinoxylan, heteroxylan or pectin. In addition, the hemicellulose for use in the processes of the invention may be a synthetic hemicellulose (i.e. a structural analogue of a naturally-occurring hemicellulose synthesised *in vitro* by any chemical/enzymic synthesis or modification).

Thus, any non-cellulosic, non-starch plant polysaccharides may be used in the process of the invention. Thus, the processes of the invention find application in the processing *inter alia* of pentosans, pectins and gums.

Some hemicelluloses are suitable as substrates for oxidative gelation ("gelling hemicelluloses"): such hemicelluloses often have substituents with phenolic groups which are cross-linkable with certain oxidizing agents. These "gelling" hemicelluloses are particularly preferred for use in the invention. Non-gelling hemicelluloses may be first derivitized with phenolic (e.g. ferulic) acid groups prior to use in the invention.

Arabinoxylans, heteroxylans and pectins may also be used. Of the arabinoxylans, particularly preferred are AXFA, AXF, AXA and AX.

Also suitable for use in the invention are pectins, including the true pectins, simple pectins, complex pectins, mesocomplex pectins and gelling pectins (e.g. those obtainable from representatives of the plant family *Chenopodiaceae*, which include beets (e.g. sugar beet), spinach and

mangelwurzels). Particularly preferred is sugar beet pectin (for example in the form of sugar beet pulp). Also useful in the invention are treated pectins (as hereinbefore defined).

The hemicellulosic material may be obtained by any of the standard techniques known in the art for obtaining hemicelluloses suitable as starting materials for oxidative gelation. Preferably, the hemicelluloses are obtained by any of the processes described in WO 93/10158.

As used herein, the term "supplement" as applied to any specified enzyme activity is intended to embrace not only the case where an appropriate enzyme preparation is added during production, but also encompasses the case where endogenous enzyme activity is activated, enhanced, induced or derepressed by any treatment (e.g. chemical or physical treatment) of the hemicellulosic material. Thus, the hemicellulosic material of the invention exhibit supplemental oxidase (and optionally peroxidase) activity howsoever achieved (so long as the level(s) of enzyme activity are sufficient e.g. to promote oxidative gelation), and are not essentially limited to hemicellulose preparations which have been prepared in any particular way.

Preferably, however, the enzyme supplement is added isolated enzyme having the desired activity. The level of purity and/or specificity is not crucial to the practise of the invention, so long as oxidase and/or peroxidase levels are elevated to levels sufficient to promote oxidative gelation under appropriate conditions.

As used herein, the term peroxidase denotes an enzyme which catalyses the general reaction:

$$H_2O_2 + H_2A \Rightarrow 2H_2O + A$$

where H_2A is any oxidisable substrate. Without wishing to be bound by any theory, it is thought that in the case of oxidative gelation the substrate is the polysaccharide/ferulic acid complex, so resulting in crosslinking between the oxidized ferulic acid components via formation of a new C-C bond and the production of diferulic acid.

Preferred according to the present invention is peroxidase EC 1.11.1.7 (e.g. horse radish peroxidase). Alternatively, naturally occurring peroxidase activity endogenous to the hemicellulose material may be exploited according to the invention.

As used herein, the term oxidase denotes an enzyme which catalyses the general reaction:

$$O_2 + AH_2 \Rightarrow H_2O_2 + A$$

where AH_2 is glucose and the enzyme glucose oxidase, the reaction is:

$$O_2 + H_2O + \text{glucose} \Rightarrow H_2O_2 + \text{gluconic acid}$$

Preferred according to the present invention is glucose oxidase EC 1.1.3.4. (e.g. A. niger as source. Other oxidases which are suitable for use in the invention include amino acid oxidases, diamine oxidases and xanthine oxidase.

The gelation system of the invention avoids the dangers associated with excess of hydrogen peroxide (which carries a risk of explosion): in the gels of the invention a "negative feedback" loop ensures that if temperature rises due to excessive hydrogen peroxide production then the enzymes producing the hydrogen peroxide are progressively denatured as the temperatures rises, so limiting the production of further hydrogen peroxide.

The gellation system of the invention also has further important and unexpected advantages which *inter alia* permit the formulation of self-felling powders or solutions.

The material of the invention may further comprising an oxidase substrate (e.g. glucose) supplement. If glucose is used, then this has the ancillary advantage of acting as a dispersant. Alternatively, endogenous substrates naturally present in the hemicellulose may be exploited.

The hemicellulosic material may be derived from any of a wide range of different starting materials. Suitable starting materials containing hemicellulose for use in the invention typically include plant material of various kinds and any part or component thereof.

Plant materials useful as a starting material in the invention include the leaves and stalks of woody and nonwoody plants (particularly monocotyledonous plants), and grassy species of the famile Gramineae. Particularly preferred are gramineous agricultural residues, i.e. the portions of grain-bearing grassy plants which remain after harvesting the seed. Such residues include straws (e.g. wheat, oat, rice, barley, rye, buckwheat and flax straws), corn stalks, corn cobs and corn husks.

Other suitable starting materials include grasses, such as prairie grasses, gamagrass and foxtail. Other suitable sources include dicotyledonous plants such as woody dicots (e.g. trees and shrubs) as well as leguminous plants.

Another preferred source are fruits, roots and tubers (used herein in the botanical sense). The term "fruit" includes the ripened plant ovary (or group thereof) containing the seeds, together with any adjacent parts that may be fused with it at maturity. The term "fruit" also embraces simple dry fruits (follicles, legumes, capsules, achenes, grains, samaras and nuts

(including chestnuts, water chestnuts, horsechestnuts etc.)), simple fleshy fruits (berries, drupes, false berries and pomes), aggregate fruits and multiple fruits. The term "fruit" is also intended to embrace any residual or modified leaf and flower parts which contain or are attached to the fruit (such as a bract). Encompassed within this meaning of fruit are cereal grains and other seeds. Also contemplated for use as starting materials are fruit components, including bran, seed hulls and culms, including malt culms. "Bran" is a component of cereals and is defined as a fraction obtained during the processing of cereal grain seeds and comprises the lignocellulosic seed coat as separate from the flour or meal. Other suitable component parts suitable as starting materials include flours and meals (particularly cereal flours and meals, and including nonwoody seed hulls, such as the bracts of oats and rice).

The term "root" is intended to define the usually underground portion of a plant body that functions as an organ of absorption, aeration and/or food storage or as a means of anchorage or support. It differs from the stem in lacking nodes, buds and leaves. The term "tuber" is defined as a much enlarged portion of subterranian stem (stolon) provided with buds on the sides and tips.

Preferred lignocellulosic starting materials include waste stream components from commercial processing of crop materials such as various beets and pulps thereof (including sugar beet pulp), citrus fruit pulp, wood pulp, fruit rinds, nonwoody seed hulls and cereal bran. Suitable cereal sources include maize, barley, wheat, oats, rice, other sources include pulses (e.g. soya), legumes and fruit.

Other suitable starting materials include pollen, bark, wood shavings, aquatic plants. marine plants (including algae), exudates, cultured tissue, synthetic gums. pectins and mucilages.

Particularly preferred as a starting material is testaceous plant material, for example waste testaceous plant material (preferably containing at least about 20% of arabinoxylan and/or glucoronoarabinoxylan).

The starting material may be treated directly in its field-harvested state or (more usually) subject to some form of pre-processing. Typical pre-processing steps include chopping, grinding, cleaning, washing, screening, sieving etc.

Preferably, the starting material is in a substantially ground form having a particle size of not more than about 100 microns. It may be air classified or sieved (for example to reduce the level of starch). Alternatively, or in addition, the starting material may be treated with enzymes to remove starch (e.g. alpha- and/or beta-amylase). The starting material may also be pre-digested with a carbohydrase enzyme to remove ß-glucan.

Suitable washing treatments include washing with hot water or acid (e.g. at a pH of 3-6, e.g. about 5). This at least partially separates protein. Other pre-treatments include protease treatment.

The hemicellulosic material may, for example, be obtained from cereal husk or bran, or legumes, e.g. from maize, wheat, barley, rice, oats or malt, though any source of hemicellulose may be used in the invention so long as it is subject to at least some degree of oxidative gelation.

Preferably, the hemicellulosic material comprises a pentosan, e.g. a water soluble or alkali soluble pentosan fraction. Particularly preferred are materials wherein the pentosan comprises arabinoxylan, for example arabinoxylan ferulate. In one preferred embodiment, the hemicellulose of the invention consists (or consists essentially) of arabinoxylan ferulate.

The material of the invention preferably takes the form of a powder,

for example a substantially anhydrous powder. Powders according to the invention preferably contain a dispersant (e.g. glucose or maltodextrin). Such powders are conveniently formulated so as to be self-gelling on the addition of water in the presence of air, for example being formulated to contain oxidase, oxidase substrate (e.g. glucose) and optionally peroxidase supplements.

The invention also contemplates the material as described herein in the form of an aqueous solution. For some applications, such aqueous solutions are preferably oxygen free and packaged in containers which effectively exclude oxygen. Such solutions may be formulated so as to be is self-gelling on exposure to oxygen (e.g. the oxygen in ambient air), for example being formulated to contain oxidase, oxidase substrate (e.g. glucose) and optionally peroxidase supplements.

Also contemplated by the invention are gels or viscous media comprising the material of the invention which has been oxidatively gelled. Such gels or viscous media may comprise (or consist essentially of) cross linked arabinoxylan.

The invention also contemplates a process for preparing a gel or viscous medium comprising the step of oxidatively gelling the materials of the invention, for example by adding water to the anhydrous self-gelling powders or by exposing the oxygen free solutions to air or oxygen.

In another aspect, the invention contemplates a process for effecting oxidative gelation of a hemicellulosic material comprising the step of promoting the generation of hydrogen peroxide *in situ* by redox enzymes.

The redox enzymes preferably comprise an oxidase (e.g. glucose oxidase) and a peroxidase (e.g. horse radish peroxidase), which are preferably present as supplements in the hemicellulosic material.

According in this aspect of the invention, the process may comprise the steps of supplementing a hemicellulosic material with an oxidase and optionally an oxidase substrate and/or a peroxidase. The generation of hydrogen peroxide is then preferably promoted by:

(a) providing oxygen to the material (e.g. by generating oxygen *in situ*); and/or

(b) providing water to the material; and/or

(c) providing oxidase substrate to the material (e.g. by generating substrate *in situ*); and/or

(d) activating one or more of the redox enzymes (e.g. chemically or physically), wherein the provision of oxygen or substrate may be by controlled release or generation *in situ*, for example triggered generation or release by heat, irradiation or chemical treatment.

Where the oxygen is provided by triggering chemical production *in situ*, the invention finds particular application in retort cooking when the gel can be induced to form only on heating.

The invention also contemplates a gel or viscous medium produced by (or obtainable by) any of the processes of the invention.

In another aspect, the invention contemplates a process for producing a hemicellulosic material comprising the step of supplementing a hemicellulose with an oxidase (e.g. glucose oxidase) and optionally a peroxidase, (e.g. horse radish peroxidase), and also contemplates materials produced by (or obtainable by) such a process.

The hemicellulose products (i.e. the gels, dehydrated gels, rehydrated dehydrated gels, gelling (but ungelled) hemicelluloses and viscous liquids of the invention find a variety of applications various therapeutic, surgical, prophylactic, diagnostic and cosmetic (e.g. skin care) applications.

For example, the aforementioned materials may be formulated as a pharmaceutical or cosmetic preparation or medical device, for example selected from: a wound plug, wound dressing, wound debriding system, controlled release device, an encapsulated medicament or drug, a lotion, cream (e.g. face cream), suppository, pessary, spray, artificial skin, protective membrane, a neutraceutical, prosthetic, orthopaedic, ocular insert, injectant, lubricant or cell implant matrix. The non-gelling, gelling and gelled hemicelluloses (e.g. AX, AXF and gelled AXF) are particularly useful as agents which maintain the integrity of the gut wall lining, and as agents for coating the luminal wall of the gastrointestinal tract. They may therefore fins particular application in animal feeds and in the treatment of gastrointestinal disorders.

In such embodiments the material, gel or viscous medium of the invention may further comprising an antibiotic, electrolyte, cell, tissue, cell extract, pigment, dye, radioisotope, label, imaging agent, enzyme, co-factor, hormone, cytokine, vaccine, growth factor, protein (e.g. a therapeutic protein), allergen, hapten or antigen (for e.g. sensitivity testing), antibody, oil, analgesic and/or antiinflammatory agent (e.g. NSAID).

Thus, the above-listed materials find application in therapy, surgery, prophylaxis or diagnosis, for example in the treatment of surface (e.g. skin or membrane lesions, e.g. burns, abrasions or ulcers). In a particularly preferred embodiment, the invention contemplates a wound dressing comprising the above listed materials of the invention, for example in the form of a spray. Such wound dressings are particularly useful for the treatment of burns, where their great moisture retaining properties help to prevent the wound drying out.

Particularly preferred for such application is a self-gelling liquid comprising gelling hemicellulose supplemented with glucose and peroxidase and/or oxidase enzymes which gels on contact with oxygen in the air. Such

compositions can be provided in the form of oxygen-free liquids in airtight containers which can be sprayed onto the skin, whereupon the liquid gels after exposure to the air. Such composition may advantageously be formulated so as to produce a slight excess of hydrogen peroxide on exposure to oxygen, so that a sterilizing, antibacterial, bacteriostatic and/or cleansing effect is obtained which helps promote healing.

The invention also contemplates water absorbent nappies, diapers, incontinence pads, sanitary towels, tampons and panty liners comprising the above-listed materials, as well as domestic and industrial cleaning or liquid (e.g. water) recovery operations (e.g. in the oil industry).

Alternatively, the gels of the invention can be provided in the form of hydrated or dehydrated sheets or pellicles for application to various internal or external surfaces of the body, for example during abdominal surgery to prevent adhesions.

Other applications include enzyme immobilizing systems, brewing adjuncts and bread improvers.

The materials listed above also find application as a foodstuff, dietary fibre source, food ingredient, additive, lubricant, supplement or food dressing. Such products are preferably selected from crumb, alginate replacer, cottage cheeses, aerosol toppings, frozen yoghurt, milk shakes, ice cream, low calorie products such as dressings and jellies, batters, cake mixes, frozen chips, binders, gravies, pastas, noodles, doughs, pizza toppings, sauces, mayonnaise, jam, preserve, pickles, relish, fruit drinks, a clouding agent in drinks, syrups, toppings and confectionary (e.g. soft centres) petfood (wherein the gel e.g. acts as a binder), a flavour delivery agent, a canning gel, fat replacer (e.g. comprising macerated gel), a coating, a glaze, a bait, a binder in meat and meat analogue products (for example vegetarian products), an edible adhesive, a gelatin replacer or dairy product

or ingredient (e.g. a yoghurt supplement).

When used as a fat replacer the gel of the invention is preferably macerated to optimize its mouthfeel and fat mimetic properties.

The ungelled (but gellable) hemicelluloses (e.g. AXF) find particular application as clouding agents (e.g. in drinks), as film forming agents (e.g. in moisture barriers), glazes, edible adhesives and other functional food ingredients.

The invention will now be described by reference to the following examples which are purely exemplary and which do not limit the scope of the invention in any way.

Example 1

1.0g of a maize-derived hemicellulosic powder prepared according to the processes described in WO 93/10158 was mixed with 0.5g of glucose and 20mg each of peroxidase and glucose oxidase (Sigma). The composition gelled at 2% in water within 5 min on shaking in air.

Example 2

0.3g of a composition prepared as described in Example 1 was mixed with 6g of Regent (heat-treated) wheat flour and dispersed as a batter (3g of flour mix in 9g of water). The product became a solid gel in about 10 min.

Example 3

1g of the flour mix prepared as described in Example 2 was mixed with a further 5g of Regent flour and dispersed as a batter (3g of flour mix

in 9g of water). The product became a solid gel in about 30 min.

Example 4

1.0g of a maize-derived hemicellulosic powder prepared according to the processes described in WO 93/10158 was mixed with 0.25g of glucose and 10mg each of peroxidase and glucose oxidase (Sigma). The composition gelled at 2% in water in 8 min on shaking in air.

Example 5

1.0g of a maize-derived hemicellulosic powder prepared according to the processes described in WO 93/10158 was mixed with 0.125g of glucose and 5mg each of peroxidase and glucose oxidase (Sigma). The composition gelled at 2% in water in 45 min on shaking in air.

Example 6

1.0g of a maize-derived hemicellulosic powder prepared according to the processes described in WO 93/10158 was mixed with 0.063g of glucose and 2.5mg each of peroxidase and glucose oxidase (Sigma). The composition gelled at 2% in water after 2 hours on shaking in air.

CLAIMS

1. A hemicellulosic material comprising an oxidase (e.g. glucose oxidase) supplement.

2. The material of claim 1 further comprising a peroxidase (e.g. horse radish peroxidase) supplement and/or an oxidase substrate (e.g. glucose) supplement.

3. The material of claim 1 or claim 2 wherein the hemicellulosic material is derived from cereal flour, husk or bran, or from legumes (e.g. from maize, wheat, barley, rice, oats or malt).

4. The material of any one of claims 1-3 wherein the hemicellulosic material comprises a pentosan, e.g. a water soluble or alkali soluble pentosan fraction.

5. The material of claim 4 wherein the pentosan comprises arabinoxylan, for example, arabinoxylan ferulate.

6. The material of claim 5 wherein the hemicellulosic material consists (e.g. consists essentially of) arabinoxylan ferulate.

7. The material of any one of the preceding claims in the form of a powder, for example a substantially anhydrous powder and optionally a dispersant (e.g. glucose or maltodextrin).

8. The material of claim 7 which comprises oxidase, oxidase substrate (e.g. glucose) and optionally peroxidase supplements, the material

being self-gelling on the addition of water.

9. The material of any one of claims 1-8 in the form of an aqueous solution.

10. The material of claim 9 which is substantially oxygen free.

11. The material of claim 10 which comprises oxidase, oxidase substrate (e.g glucose) and optionally peroxidase supplements and which is self-gelling on exposure to oxygen.

12. A gel or viscous medium comprising the material of any one of claims 1-11 which has been oxidatively gelled.

13. The gel of claim 12 wherein the material comprises (or consists essentially of) cross linked arabinoxylan.

14. The gel of viscous medium of claim 12 or 13 in dehydrated form.

15. The dehydrated gel or viscous medium of claim 14 in rehydrated form.

16. A process for preparing a gel or viscous medium comprising the step of oxidatively gelling the material of any one of claims 1-11, for example by adding water to the material of claim 8 or by exposing the material of any one of claims 9-11.

17. A process for effecting oxidative gelation of a hemicellulosic material comprising the step of promoting the generation of hydrogen peroxide *in situ* by redox enzymes.

18. The process of claim 16 wherein the redox enzymes comprise an oxidase (e.g. glucose oxidase) and a peroxidase (e.g. horse radish

peroxidase).

19. The process of claim 17 or 18 wherein the process comprises the steps of supplementing a hemicellulosic material with an oxidase and optionally an oxidase substrate and/or a peroxidase.

20. The process of any one of claims 17-19 wherein the generation of hydrogen peroxide is promoted by:

(a) providing oxygen to the material (e.g. by generation or release *in situ*); and/or

(b) providing water to the material; and/or

(c) providing oxidase substrate to the material (e.g. by generation or release *in situ*); and/or

(d) activating one or more of the redox enzymes (e.g. chemically or physically),

wherein the provision of oxygen or substrate may be by controlled release or generation *in situ*, for example by triggered generation or release by heat, irradiation or chemical treatment(s).

21. A gel or viscous medium produced by (or obtainable by) the process of any one of claims 16-20.

22. A process for producing a hemicellulosic material (for example a material according to any one of claims 1-11) comprising the step of supplementing a hemicellulose with an oxidase (e.g. glucose oxidase) and optionally a peroxidase (e.g. horse radish peroxidase) supplement.

23. A material produced by (or obtainable by) the process of claim 22.

24. A pharmaceutical or cosmetic preparation or medical device

comprising the material, gel, viscous medium, dehydrated gel/viscous medium of any one of the preceding claims, the preparation or device being for example selected from: a wound plug, wound dressing, controlled release device, an encapsulated medicament or drug, a lotion, cream, suppository, pessary, spray, artificial skin, protective membrane, a neutraceutical, prosthetic, orthopaedic, ocular insert, injectant, lubricant or cell implant matrix, optionally further comprising an antibiotic, analgesic and/or antiinflammatory agent.

25. The material, gel or viscous medium of any one of the preceding claims for use in therapy, prophylaxis or diagnosis, for example in the treatment of skin lesions (e.g. burns, abrasions or ulcers).

26. A wound dressing comprising the material of claim 11, for example in the form of a spray.

27. A bread improver comprising the material, gel or viscous medium of any one of the preceding claims.

28. A foodstuff, dietary fibre source, food ingredient, additive, lubricant, supplement or dressing comprising the material of any one of claims, the gel or viscous medium of any one of claims, for example being selected from a petfood (wherein the gel e.g. acts as a binder), a flavour delivery agent, a canning gel, fat replacer (e.g. comprising macerated gel of any one of the preceding claims), a coating, a glaze, a bait or a gelatin replacer.

29. A masking agent comprising the gel of any one of the preceding claims, for example for use in masking semiconductor wafers, etching plates or surfaces to be painted.

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

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Date of mailing (day/month/year) 02 July 1998 (02.07.98)	
International application No. PCT/GB97/03140	**Applicant's or agent's file reference** P56885P
International filing date (day/month/year) 14 November 1997 (14.11.97)	**Priority date** (day/month/year) 21 November 1996 (21.11.96)
Applicant FITCHETT, Colin, Stanley	

1. The designated Office is hereby notified of its election made:

[X] in the demand filed with the International Preliminary Examining Authority on:

05 June 1998 (05.06.98)

[ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was

[ ] was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO **34, chemin des Colombettes** **1211 Geneva 20, Switzerland**	Authorized officer F. Zotomayor
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38

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NOTIFICATION OF THE RECORDING OF A CHANGE

(PCT Rule 92bis.1 and Administrative Instructions, Section 422)

From the INTERNATIONAL BUREAU

To:

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Fry Heath & Spence
The Old College
53 High Street
Horley
Surrey RH6 7BN
ROYAUME-UNI

Date of mailing (day/month/year)
08 January 1999 (08.01.99)

Applicant's or agent's file reference
P56885P

IMPORTANT NOTIFICATION

International application No.
PCT/GB97/03140

International filing date (day/month/year)
14 November 1997 (14.11.97)

1. The following indications appeared on record concerning:

[X] the applicant [ ] the inventor [ ] the agent [ ] the common representative

Name and Address
DALGETY PLC
100 George Street
London W1H 5RH
United Kingdom

State of Nationality: GB
State of Residence: GB
Telephone No.:
Facsimile No.:
Teleprinter No.:

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

[X] the person [ ] the name [ ] the address [ ] the nationality [ ] the residence

Name and Address
E.I. DUPONT DE NEMOURS AND COMPANY
1007 Market Street
Wilmington, DE 19898
United States of America

State of Nationality: US
State of Residence: US
Telephone No.:
Facsimile No.:
Teleprinter No.:

3. Further observations, if necessary:

4. A copy of this notification has been sent to:

[X] the receiving Office
[ ] the International Searching Authority
[ ] the International Preliminary Examining Authority
[ ] the designated Offices concerned
[X] the elected Offices concerned
[ ] other:

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer
Ting Zhao

Telephone No.: (41-22) 338.83.38

Form PCT/IB/306 (March 1994)

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